THE EXPERIMENTAL DETERMINATION OF THE P-V-T-X RELATIONS FOR THE CARBON DIOXIDE-NITROGEN AND THE CARBON DIOXIDE-METHANE SYSTEMS

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The P-V-T-X relations around the phase boundaries have been measured for the carbon dioxide-nitrogen and the carbon dioxide-methane systems. A visual glass capillary was used as the equilibrium cell. The principle of the experimental procedure is based on the dew and bubble point method. The pressure range covered was from 20 to 150 atm and the experimental temperatures were 15°C, 0°C and -20°C. From the data obtained, compressibility factor charts were constructed for the entire experimental range. The fugacities and partial molar volumes were also calculated.

Introduction

Volumetric data in addition to pressure-temperature-composition relations are essentials for development of the theory of phase equilibrium. However, relatively few publications concerning P-V-T-X relations can be found in the literature. This may be attributed to the difficulty of experimental work. Outstanding work on these relations has been carried out by Sage and Lacey and by Kay.

In this study, experimental determination of P-V-T-X relations was carried out for the CO₂-N₂ and the CO₂-CH₄ systems, whose components are practically nonpolar or slightly polar. The purpose of this investigation was to provide a comprehensive set of experimental data for the aforementioned systems, and these are presented here. A further object was to compare the measured data with a solution model made on the basis of statistical thermodynamics. This comparison has been made and will be published elsewhere.

The experimental method employed here was a visual glass capillary method which was almost the same as that used by Kay, though some improvements were made in introducing sample gas into the equilibrium cell. From the data obtained, compressibility factor charts are presented for the entire experimental range. The fugacities and partial molar volumes were also calculated.

Experimental Apparatus and Procedure

The procedure used here was based on the dew and bubble point method. Briefly, the method consisted of introducing a known amount of gas mixture, whose composition was predetermined, into a glass capillary cell maintained at a constant temperature. The content of the equilibrium cell was slowly compressed with mercury supplied from a pump so that, as the pressure was raised, the system passed successively and isothermally through the states of unsaturated vapor, saturated vapor, mixed vapor and liquid, saturated liquid and finally single-phase liquid. This procedure was repeated with a series of different compositions and at different temperatures to determine the P-V-T-X relations of the systems, CO₂-N₂ and CO₂-CH₄.

A schematic diagram of the apparatus used is shown in Fig. 1. The Pyrex equilibrium cell, shown in detail in Fig. 2, is 300 mm long with an I.D. of 2.6 mm and an O.D. of 9 mm. The equilibrium cell was carefully calibrated for volume throughout its length by being filled to various levels with mercury. The calibration for the total volume of the cell was accurate to ± 0.001 cc. The cell contained a small steel ball which could be raised or lowered by an external magnet. The volume of the ball was determined to be 0.007 cc by measuring its average diameter. Rapidly raising and lowering the ball provided good agitation in the cell.

To introduce a proper amount of gas mixture into the cell at low pressure, a glass burette was connected
Fig. 1 Schematic diagram of the experimental apparatus

Fig. 2 Details of the equilibrium cell and glass burette

1. Sample gas bomb
2. Mercury manometer
3. Vacuum pump
4. Toeppler pump
5. Mercury
6. U-shaped glass burette
7. Glass burette
8. Glass burette
9. Air bomb
10. Gas holder
11. Mercury holder
12. Cock
13. Three-way valve
14. Glass tube window
15. Regulator
16. Glass burette contained in stainless steel cylinder (cf. Fig. 2)
17. Glass burette
18. Bath packed with urethane foam rubber
19. Motor
20. Mercury level meter
21. Dead-weight gage
22. Oil pump
23. Mercury pump
24. Bourdon gage
25. 114 ( 2 ) JOURNAL OF CHEMICAL ENGINEERING OF JAPAN

at the bottom of the cell as shown in Fig. 2. The volume of the burette was about 25 cc. The burette was covered with a cylinder made of stainless steel and was prevented from bursting at above 50 atm by balancing the pressure between the inside and the outside of the burette. The pressure of the outside could be arbitrarily changed by compressed air introduced from a bomb. The connection of glass to steel was made by a commercial adhesive, "Araldite".

The equilibrium cell was placed in a constant-temperature bath which had glass windows (450 mm x150 mm) fixed at front and back of the bath. The temperature of the bath was controlled at 15°C, 0°C and -20°C, ±0.01°C for each run.

The pressure inside the equilibrium cell was measured by a dead-weight gage. The details and calibration method for the gage were described elsewhere. Pressure balance between the equilibrium cell and the dead-weight gage was detected by
observing the positions of oil and mercury. The oil-
mercury interface in the connection of the oil pump
and the mercury pump was detected electrically. Two
probes were inserted between the surfaces of the
oil and the mercury which were stored in a cham-
ber made of stainless steel. The chamber is shown
in Fig. 1, as number 2. Hereafter elements of the
apparatus will be denoted by the numbers shown
in Fig. 1. The distance between the probes was about
5 mm and they were insulated from the chamber by
fixing them with an adhesive, "Araldite". By an
alternative handling of the oil pump, 2, and the
mercury pump, 3, it is easy to control the oil-
mercury interface within this range throughout the
experiment.

The position of the mercury in the equilibrium
cell, which changed according to pressure, was
measured by a cathetometer through the glass window.
The vapor pressure of the mercury was neglected
because experimental temperatures were sufficiently
low. After all corrections, the accuracy of pressure
measurement was within ± 0.01 atm.

Materials used The nitrogen used was stated
to be 99.99% pure, and was furnished by the Nippon
Sanso Industry Co., Ltd. The methane and carbon
dioxide were provided by the Takachiho Chemical
Industry Co., Ltd. and the Showa Tansan Industry
Co., Ltd. and their purities were reported to be more
than 99.64% and more than 99.9%, respectively.

Preparation of mixtures A sample gas of known
composition was prepared in the following manner
(see Fig.1). First, the whole of the apparatus was
vacuated with a vacuum pump. It was then
ascertained by using a manometer, 2, that there
were no leaks anywhere. Each component of an
aimed binary system was introduced slowly into
the glass burettes, 7 and 8, individually. Each glass
bulb of the burette was about 14 cc. The calibra-
tion for the bulb was carried out with mercury and
accuracy was within ± 0.01 cc. The burettes re-
spectively consisted of ten bulbs and their total
volumes were about 140 cc. After charging one
component, the gas remaining in the pipe line was
withdrawn by a vacuum pump and the other
component gas was introduced. The U-shaped
glass burette, 6, whose total volume was 36 cc, was
prepared to measure the volume of small amounts
of sample. The sample was mixed by displacing it
from the burette, 7, to the burette, 8, and then from
8 to 7 with mercury. So that it should mix better,
the sample was allowed to stand for half a day after
this agitation. A sample of about 40 cc at atmosphere
was provided for the measurement in the unsaturated
vapor region. For measuring the other regions,
samples of about 100 cc were prepared.

Filling the equilibrium cell with sample The
well-mixed sample was first displaced into the gas
holder, 6, by holding mercury in the burettes, 7 and
8, up to their cocks. The cock, 8, was then closed
and the sample was introduced into the equilibrium
cell through the three-way valve, 8. This was per-
fomed by using the mercury stored in the mercury
holder, 4. Mercury was pressed up to the neck of the
gas holder by compressed air supplied from a
bomb. The three-way valve was then closed and the
outlet to the gas holder was shut. The sample was
slowly charged with mercury supplied from a pump,
8, through the three-way valve, the glass burette
covered with a cylinder and finally into the equilib-
rium cell. The interface between the sample and
the mercury was previously detected through the
glass tube window, 9. The sample remaining in the
stainless tube, valves and burettes was returned to the
U-shaped glass burette by using a Toeppler pump, 4.
This amount was subtracted from the initial total mole
and the net mole of the sample charged into the equi-
librium cell was finally determined.

Determination of dew and bubble points The
P–V–T–X relations were determined by compressing
the content in the equilibrium cell under various pres-
ures. The volume of the content was measured by
observing the length from the top of the capillary to
the meniscus of the mercury. The length was mea-
sured by means of a cathetometer and the necessary
correction for mercury meniscus was made in the final
determination of volume. Near the dew point, liquid
film on the surface of the equilibrium cell was ob-
served with the aid of a light through the glass
window. The presence of liquid film was recognized
by a dark spot occurring when the steel ball contacted
the wall. Near the bubble point, a pressure change
of about 38 mmHg made a small bubble of gas disap-
pear and reappear at the top of the equilibrium cell.
These observations have been reported by Cummings
et al.3 and by Kay4. To prevent the arbitrariness
of determination by the eye, graphical analyses of the
data were also used to determine those points. The
plots of molar volumes against pressures presented
break points at dew and bubble points (for typical
plots, see Fig. 3).

Experimental Results and Discussion

To test the validity of this method, the present data
were compared with those of other workers3,6,8,9.
A comparison is made in Figs. 4 and 5 of the P–X and
P–V relations at phase equilibrium of the CO2–N2
system determined by the static and circulation
methods. They agree very well, as shown in Figs.
4 and 5. The data obtained here are summarized
in Tables 1 to 4. The use of mercury prevented
further measurements at lower temperatures.

By using these data we constructed compressibil-
ity factor charts over the entire experimental range.
They are presented in Figs. 6 to 9. The fugacities
and partial molar volumes of liquid phase under phase
equilibrium are also presented, in Figs. 10 to 17.
They were calculated by the following equations:

For fugacity

\[ f_i = \phi_i y_i P \]
Fig. 3  P-V relations of CO₂-CH₄ (X_CH₄ = 0.129) near the bubble and dew points at 0°C

Fig. 4  P-X relation of CO₂-N₂ at 0°C

Fig. 5  P-V relation of CO₂-N₂ at 0°C

Fig. 6  Compressibility factor of CO₂-N₂ at 15°C

Fig. 7  Compressibility factor of CO₂-N₂ at 0°C

Fig. 8  Compressibility factor of CO₂-CH₄ at 15°C
<table>
<thead>
<tr>
<th>CO₂ – N₂; Temp. = 15°C</th>
<th>CO₂ – CH₄; Temp. = 15°C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dew</strong></td>
<td><strong>Bubble</strong></td>
</tr>
<tr>
<td><strong>X</strong></td>
<td><strong>P</strong></td>
</tr>
<tr>
<td>0.000</td>
<td>50.3</td>
</tr>
<tr>
<td>0.060</td>
<td>56.2</td>
</tr>
<tr>
<td>0.103</td>
<td>61.7</td>
</tr>
<tr>
<td>0.132</td>
<td>66.5</td>
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<tr>
<td>0.155</td>
<td>70.9</td>
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<tr>
<td>0.173</td>
<td>74.9</td>
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<tr>
<td>0.188</td>
<td>80.0</td>
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<tr>
<td>0.194</td>
<td>82.2</td>
</tr>
<tr>
<td>0.199</td>
<td>84.0</td>
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<tr>
<td>0.202</td>
<td>89.5</td>
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</table>

<table>
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<th>CO₂ – N₂; Temp. = 0°C</th>
<th>CO₂ – CH₄; Temp. = 0°C</th>
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</thead>
<tbody>
<tr>
<td><strong>Dew</strong></td>
<td><strong>Bubble</strong></td>
</tr>
<tr>
<td><strong>X</strong></td>
<td><strong>P</strong></td>
</tr>
<tr>
<td>0.000</td>
<td>34.5</td>
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<tr>
<td>0.071</td>
<td>38.6</td>
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<tr>
<td>0.128</td>
<td>42.5</td>
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<tr>
<td>0.254</td>
<td>56.6</td>
</tr>
<tr>
<td>0.306</td>
<td>65.2</td>
</tr>
<tr>
<td>0.367</td>
<td>86.4</td>
</tr>
<tr>
<td>0.434*</td>
<td>114.7</td>
</tr>
<tr>
<td>0.534*</td>
<td>129.4</td>
</tr>
<tr>
<td>0.568*</td>
<td>114.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CO₂ – N₂; Temp. = −20°C</th>
<th>CO₂ – CH₄; Temp. = −20°C</th>
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</thead>
<tbody>
<tr>
<td><strong>Dew</strong></td>
<td><strong>Bubble</strong></td>
</tr>
<tr>
<td><strong>X</strong></td>
<td><strong>P</strong></td>
</tr>
<tr>
<td>0.000</td>
<td>23.9</td>
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<tr>
<td>0.017</td>
<td>25.1</td>
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<td>0.243</td>
<td>28.7</td>
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<tr>
<td>0.347</td>
<td>35.9</td>
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<tr>
<td>0.434</td>
<td>46.9</td>
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<tr>
<td>0.534*</td>
<td>129.4</td>
</tr>
<tr>
<td>0.568*</td>
<td>114.0</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>CO₂ – N₂; Temp. = −20°C</th>
<th>CO₂ – CH₄; Temp. = −20°C</th>
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<tbody>
<tr>
<td><strong>Dew</strong></td>
<td><strong>Bubble</strong></td>
</tr>
<tr>
<td><strong>X</strong></td>
<td><strong>P</strong></td>
</tr>
<tr>
<td>0.000</td>
<td>41.5</td>
</tr>
<tr>
<td>0.129</td>
<td>56.4</td>
</tr>
<tr>
<td>0.220</td>
<td>92.0</td>
</tr>
<tr>
<td>0.276</td>
<td>84.1</td>
</tr>
<tr>
<td>0.321</td>
<td>64.2</td>
</tr>
<tr>
<td>0.321*</td>
<td>84.1</td>
</tr>
<tr>
<td>0.340</td>
<td>82.7</td>
</tr>
<tr>
<td>0.340*</td>
<td>74.9</td>
</tr>
<tr>
<td>0.349</td>
<td>81.7</td>
</tr>
</tbody>
</table>

**Table 1** Dew and bubble points of CO₂-N₂ and CO₂-CH₄

**Unit:** P = atm  V = cc/g-mole  X = mole fraction of N₂ or CH₄

* retrograde condensation point
** critical opalescence was clearly observed
Fig. 9 Compressibility factor of CO₂-CH₄ at 0°C

Fig. 10 Fugacities of CO₂ and N₂ at phase equilibrium at 15°C

Fig. 11 Fugacities of CO₂ and N₂ at phase equilibrium at 0°C
Table 3  P-V-T-X relation of CO₂-CH₄ in gas region

\[ \text{Temp. = } 15°C \]

<table>
<thead>
<tr>
<th>X = 0.058</th>
<th>X = 0.098</th>
<th>X = 0.137</th>
<th>X = 0.167</th>
<th>X = 0.177</th>
<th>X = 0.182</th>
<th>X = 0.247</th>
<th>X = 0.300</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>V</td>
<td>P</td>
<td>V</td>
<td>P</td>
<td>V</td>
<td>P</td>
<td>V</td>
</tr>
<tr>
<td>24.0 839</td>
<td>24.0 843</td>
<td>24.0 859</td>
<td>24.0 857</td>
<td>24.0 857</td>
<td>24.0 857</td>
<td>24.0 857</td>
<td>24.0 857</td>
</tr>
<tr>
<td>29.5 652</td>
<td>29.5 656</td>
<td>29.5 667</td>
<td>29.5 672</td>
<td>29.5 672</td>
<td>29.5 672</td>
<td>29.5 672</td>
<td>29.5 672</td>
</tr>
<tr>
<td>33.3 557</td>
<td>33.3 562</td>
<td>37.2 497</td>
<td>104.8 612</td>
<td>37.2 503</td>
<td>104.8 612</td>
<td>37.2 503</td>
<td>104.8 612</td>
</tr>
<tr>
<td>41.0 416</td>
<td>41.0 424</td>
<td>44.8 382</td>
<td>124.1 56.8</td>
<td>44.8 389</td>
<td>124.1 56.8</td>
<td>44.8 389</td>
<td>124.1 56.8</td>
</tr>
<tr>
<td>46.7 314</td>
<td>46.7 324</td>
<td>52.5 296</td>
<td>143.4 54.6</td>
<td>52.3 305</td>
<td>143.4 55.4</td>
<td>52.3 305</td>
<td>143.4 55.4</td>
</tr>
<tr>
<td>52.5 270</td>
<td>56.3 244</td>
<td>60.2 227</td>
<td>69.3 169</td>
<td>69.3 169</td>
<td>69.3 169</td>
<td>69.3 169</td>
<td>69.3 169</td>
</tr>
</tbody>
</table>

Table 4  P-V-T-X relation of CO₂-N₂ and CO₂-CH₄ in liquid region

\[ \text{Temp. = } 15°C \]

<table>
<thead>
<tr>
<th>CO₂-N₂</th>
<th>CO₂-CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>X = 0.000</td>
<td>X = 0.060</td>
</tr>
<tr>
<td>P</td>
<td>V</td>
</tr>
<tr>
<td>53.5 52.5</td>
<td>81.5 55.2</td>
</tr>
<tr>
<td>66.4 51.0</td>
<td>89.5 53.8</td>
</tr>
<tr>
<td>104.8 48.6</td>
<td>97.1 52.7</td>
</tr>
<tr>
<td>120.2 47.8</td>
<td>104.8 51.7</td>
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<tr>
<td>143.3 46.8</td>
<td>116.3 50.7</td>
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<tr>
<td>131.7 48.6</td>
<td>133.6 52.6</td>
</tr>
<tr>
<td>135.6 49.2</td>
<td>143.3 51.8</td>
</tr>
</tbody>
</table>

\[ \text{Temp. = } 0°C \]

| X = 0.000       | X = 0.071    | X = 0.128 | X = 0.254 |
| P    | V    | P    | V    | P    | V    | P    | V    |
| 48.4 45.1       | 73.0 48.3    | 97.1 51.1 | 118.6 66.0 |
| 74.0 44.2       | 89.4 47.1    | 101.0 50.6 | 120.1 65.0 |
| 89.4 43.8       | 112.4 46.3   | 104.7 50.4 | 127.8 62.2 |
| 112.3 43.1      | 120.1 45.7   | 112.4 49.8 | 135.5 58.7 |
| 120.0 42.5      | 127.8 45.4   | 123.9 48.9 | 143.2 58.5 |
| 143.2 42.0      | 143.2 44.5   | 143.2 47.2 |

\[ V = x_1 \bar{v}_1 + x_2 \bar{v}_2 \quad (6) \]

Table 5  P-V-T-X relation of CO₂-CH₄ in liquid region

\[ \text{Temp. = } 15°C \]

| X = 0.043       | X = 0.091    | X = 0.116  | X = 0.146  |
| P    | V    | P    | V    | P    | V    | P    | V    |
| 74.2 53.0       | 81.9 57.2    | 81.9 62.4 | 89.6 66.2 |
| 89.6 51.2       | 89.6 55.7    | 89.6 59.5 | 104.8 60.7 |
| 104.8 50.0      | 104.8 53.4   | 104.8 56.2 | 124.1 57.0 |
| 124.1 46.8      | 124.1 51.5   | 124.1 53.7 | 143.4 54.8 |
| 143.4 48.8      | 143.4 50.1   | 143.4 52.0 |

\[ \text{Temp. = } 0°C \]

| X = 0.129       | X = 0.220    | X = 0.276  |
| P    | V    | P    | V    | P    | V    |
| 70.2 52.2       | 81.7 62.1    | 85.6 72.8 |
| 77.9 51.4       | 89.4 59.1    | 93.3 66.4 |
| 89.8 50.3       | 104.7 56.2   | 104.7 61.9 |
| 103.8 49.2      | 120.1 53.9   | 120.1 58.5 |
| 123.9 48.1      | 131.6 53.0   | 131.7 56.7 |
| 143.2 47.6      | 143.2 52.0   | 143.2 55.4 |

\[ \text{Unit: } P = \text{atm} \quad V = \text{cc}/\text{g-mole} \quad X = \text{mole fraction of CH}_4 \]

\[ \phi_1 = \ln \left( \frac{x_1}{1-x_1} \right) + \frac{1}{x_1} \frac{\partial \ln P}{\partial T} \quad (2) \]

\[ \phi_m = \ln \left( \frac{x_1}{x_2} \right) + x_2 \ln \phi_2 \quad (3) \]

\[ \phi_m = \int \left( x_2 \frac{\partial P}{\partial T} \right) \frac{
abla P}{x_2} \text{d}P \quad (4) \]

\[ \bar{v}_1 = V - x_1 \left[ \frac{\partial V}{\partial T} \bigg|_{T} - \frac{\partial V}{\partial P} \bigg|_{T} \right] \quad (5) \]

\[ V = x_1 \bar{v}_1 + x_2 \bar{v}_2 \quad (7) \]

\[ \text{where} \]

\[ \ln \phi_1 = \ln \phi_m + x_2 \left( \frac{\partial \ln \phi_m}{\partial T} \right)_{P,T} \]

\[ \ln \phi_m = \ln x_1 + \ln \phi_2 \]

\[ \ln \phi_m = \int \left( x_2 \frac{\partial P}{\partial T} \right) \frac{
abla P}{x_2} \text{d}P \]

\[ \bar{v}_1 = V - x_1 \left[ \frac{\partial V}{\partial T} \bigg|_{T} - \frac{\partial V}{\partial P} \bigg|_{T} \right] \]
Fig. 12 Fugacities of CO₂ and CH₄ at phase equilibrium at 15°C

Fig. 13 Fugacities of CO₂ and CH₄ at phase equilibrium at 0°C

Fig. 14 Partial molar volumes of CO₂ and N₂ at phase equilibrium at 15°C

Fig. 15 Partial molar volumes of CO₂ and N₂ at phase equilibrium at 0°C

Fig. 16 Partial molar volumes of CO₂ and CH₄ at phase equilibrium at 15°C

Fig. 17 Partial molar volumes of CO₂ and CH₄ at phase equilibrium at 0°C
binary systems studied here. That is to say, there is a straight-line relationship between pressure and average density of coexisting liquid and vapor. This is illustrated in Figs. 18 to 20. This relation held in all cases in this study except for a slight discrepancy near the critical point for the CO₂-CH₄ system at −20°C as shown in Fig. 20. The point of intersection of the rectilinear diameter with the coexisting curve gives the critical density and pressure. The critical composition was also determined graphically by using another straight-line correlation as shown in Figs. 21 and 22. By extrapolating the line to the critical pressure, the critical composition is obtained. The critical points determined are presented in Table 5.

### Table 5 Extrapolated critical values of CO₂-N₂ and CO₂-CH₄

<table>
<thead>
<tr>
<th>System</th>
<th>t [°C]</th>
<th>xᶜ [-]</th>
<th>pᶜ [atm]</th>
<th>vᶜ [cc/g-mole]</th>
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</thead>
<tbody>
<tr>
<td>CO₂-N₂</td>
<td>15</td>
<td>0.162</td>
<td>96.8</td>
<td>80.4</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0.280</td>
<td>117.2</td>
<td>72.9</td>
</tr>
<tr>
<td></td>
<td>−20</td>
<td>0.395</td>
<td>142.5</td>
<td>63.4</td>
</tr>
<tr>
<td>CO₂-CH₄</td>
<td>15</td>
<td>0.166</td>
<td>80.5</td>
<td>85.5</td>
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<td>0</td>
<td>0.300</td>
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<td>0.475</td>
<td>82.4</td>
<td>79.8</td>
</tr>
</tbody>
</table>

Unit: xᶜ = mole fraction of N₂ or CH₄
in Table 5. The values of critical pressure and temperature for the CO₂-CH₄ system agreed well
with those of Donnelly and Katz², though a slight discrepancy was shown for the critical pressure at a
low concentration of methane.

Nomenclature

\[ f = \text{fugacity} \]
\[ d = \text{density} \] [atm]
\[ P = \text{pressure of system} \] [g/cc]
\[ T = \text{temperature} \] [°K]
\[ V = \text{molar volume of system} \] [cc/g-mole]
\[ \psi_i = \text{partial molar volume of component } i \] [cc/g-mole]
\[ X = \text{mole fraction of light component of system} \]
\[ x = \text{mole fraction of liquid} \]
\[ y = \text{mole fraction of vapor} \]
\[ z = \text{compressibility factor} \]
\[ \phi = \text{fugacity coefficient} \]

(<Subscripts and superscripts>

1,2 = component 1 and 2

Literature cited


ACTIVITY COEFFICIENTS AT INFINITE DILUTION
FOR TERNARY SYSTEM

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Thermodynamically exact equations are derived for determining the infinite dilution ternary activity coefficients in liquid phase from isothermal total pressure-concentration data \((P-x)\) and from isobaric bubble temperature-concentration data \((T-x)\), respectively, for a ternary system.

Knowledge of the ternary activity coefficients in liquid phase at infinite dilution is important for the design of distillation equipment, especially for the proper choice of solvents in extractive and azeotropic distillations, or to discuss the effect of a small amount of a component in a mixture on the distillation technique.

For infinite dilution ternary activity coefficients, however, there has been only the work done by B.-Meisenheimer and Kortüm¹, who proposed an approximate expression, a modification of the one proposed by Carlson and Colburn for binary systems.

It is the object of this paper to derive thermodynamically exact equations for determining the infinite dilution ternary activity coefficients in liquid phase from \(P-x\) and \(T-x\) data, respectively, and to illustrate the use of these equations.

Theory

The activity coefficient of component \(i\) at infinite dilution as in a system is defined as follows:

\[
\gamma_i^{\text{IL}} = \lim_{x_i \to 0} \frac{\gamma_i}{f_i^{\text{IL}}} \frac{T_i}{T}\]

At the vapor-liquid equilibrium condition,

\[
\gamma_i^{\text{IL}} = \left( \frac{f_i^{\text{IL}}}{f_i} \right) \frac{y_i}{x_i}
\]

As \(x_i\) approaches zero, \(y_i/x_i\) approaches 0/0.